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Processing of composites in the Ti-Si-C system

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New composites utilizing Ti_3SiC_2 as the matrix phase have been synthesized. The thermal and kinetic aspects of the phase formation in the Ti-Si-C system were examined. Standard dry powder processing techniques, pressureless sintering and hot pressing (both under inert atmosphere) were employed to process the sample materials. The phase identification was performed by X-ray powder diffraction (XRPD) analysis. The ratio of the volume fractions of the reinforcement phases SiC and/or TiC_x to the matrix phase Ti_3SiC_2 have been measured and tailored over a wide range by means of controlling the stoichiometry of the starting elemental powders and varying the heat treatment. It was found that the Si tends to evaporate at elevated temperatures during sintering. The loss of Si is the likely reason why it is difficult to form the single phase Ti_3SiC_2. Incorporating this observation into the composite formation, a method to form in-situ composites is proposed. The volume fraction of the constituent phase in the composite can be controlled by varying the processing parameters. © *2001 Kluwer Academic Publishers*

1. Introduction

Ti_3SiC_2 has been characterized as both a metal and a ceramic, owing to its hexagonal structure. As a result, this ternary compound has recently received much attention. Many methods have been tried and reported in literature to produce this compound. Among the most successful are chemical vapor deposition (CVD) [1], solid combustion [2], hot-isostatic-pressing and self-propagating high temperature synthesis (HIP-SHS) [3], and solid state reactions using elemental species and carbides (SiC or TiC) [4–7]. Some of these methods are considered expensive or form secondary phases. At least one minor phase, TiC_x, is almost always present together with the desired titanium silicon carbide, Ti_3SiC_2. The reason for this has remained unclear [2].

Ti_3SiC_2, adopts hexagonal symmetry, with planar Si layers linked together by Ti_6C octahedrons. It has lattice constants of about $a = 3.068$ and $c = 17.668$ Å ($P6_3/mmc$, space group 194) [1, 3, 8–11], and density of 4.53 g/cm^3 [1, 8]. In addition to its normal ceramic characteristics, Ti_3SiC_2 shows some metallic behavior [1–4, 6, 9, 10]. This observation has triggered significant interest in this material. However, the pure phase has only been successfully synthesized on a lab scale, attempts to make large amounts of Ti_3SiC_2 often contain TiC_x or SiC impurities [2–7, 10].

The first phase relation study on the Ti-Si-C, among other Me-Si-C and Me-Si-N systems (where Me = Ti, Zr, Ce and Nb), was reported by Brewer and Krikorian [12] in 1956. A tentative phase diagram at about 2000°K was proposed. Apart from five binary compounds of no solubility (three of them ($TiSi_2$, TiSi, Ti_5Si_3) in Ti-Si, one (TiC) in Ti-C and one (SiC) in Si-C binary system), they did not observe the formation of any ternary compounds.

Bruckl [13] found that two ternary compounds (T1 and T2) existed in the Ti-Si-C system in his studies of the phase relations at 1200°C. T1 has the composition of Ti_3SiC_2 and that of T2 is close to Ti_5Si_3. He also found that there is certain carbon and silicon solubility in β-Ti and carbon deficiency in TiC. In the latter case, TiC_{1-x} was suggested as the composition formula. In addition, an extra line compound of composition Ti_5Si_4 was reported. However, Bruckl's diagram was hard to interpret thermodynamically in the region of Ti_5Si_3-T2.

Several modifications were made after Bruckl's work, partially owing to the unique properties of the ternary phase Ti_3SiC_2 (T1), which appeared to be have a combination of metallic and ceramic character. Ratliff and Powell [14] discovered that the Ti_5Si_3 phase has a large solubility for carbon and silicon and therefore renamed it as $Ti_5Si_3C_x$. In their 1200°C section, the T2 phase was eliminated, as was the thermodynamic violation. Furthermore, they found considerable carbon and silicon solubility in β-Ti and Ti_3SiC_2.

Not aware of Ratliff and Powell's revision, Wakelkamp *et al.* [15] made two more isothermal sections for the Ti-Si-C system. In both cases, considerable

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solubility was found in β-Ti, Ti_5Si_3 and Ti_3SiC_2 (T1). The shape of the T2 phase was corrected to ensure that the thermodynamic rules are obeyed. At the low temperature section of 1100°C, Ti_3Si was found but readily decomposed upon exposure to either carbon or oxygen. The Ti_3Si phase was not found at 1250°C.

Focusing on material behavior under high pressures (1 to 2 GPa), Sambasivan and Petuskey [16] studied the phase relationships of the Ti-Si-C system in the temperature region of 1200 to 1500°C. Using diffusion couples of Ti and SiC they proposed an isothermal section at 1200°C under pressure >2.4 GPa. Their diagram is similar to Ratliff and Powell's modification with one exception; they added the Ti_3SiC_z phase and its corresponded phase regions.

Recently, Arunajatesan and Carim [17] re-modified the 1200°C section, taking the previous work into consideration (but did not mention the two isothermal sections of Wakelkamp *et al.*). The only change they made is the extension of the solubility limits in the ternary compound Ti_3SiC_2. Fig. 1 shows their phase diagram with our compositions marked on it. Besides the ternary compound Ti_3SiC_2, there are six binary compounds available (Ti_3Si was excluded). Many of them can be used as reinforcements with Ti_3SiC_2 as the potential matrix. Tong *et al.* have tried to make composites of Ti_3SiC_2/SiC and SiC/TiC using commercial Ti, TiC, Si, β-SiC powders by hot pressing [18, 19]. They found considerable amount of secondary phases present in their final products. There was about 8 vol% TiC in the composite of Ti_3SiC_2/SiC and a small amount of elemental C, Si and the ternary compound Ti_3SiC_2 in the composite of SiC/TiC.

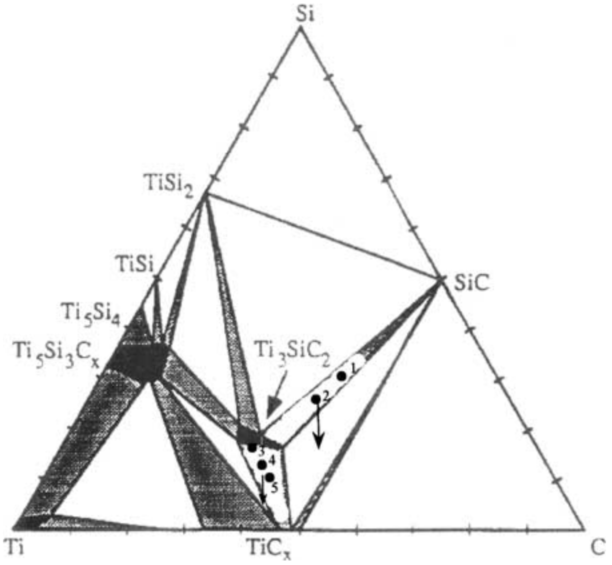


Figure 1 Phase diagram of the Ti-Si-C system at 1200°C (after Ref. 17). Reprinted with permission of the American Ceramic Society, Post Office Box 6136, Westerville, Ohio, 43086-6136.

We have attempted to make *in-situ* composites by reactive sintering in the Ti-Si-C system. Utilizing the available phase diagram information (see Fig. 1), one should be able to produce composites of desired volume fractions. The objective of this study was therefore to make composites by solid state reaction starting with elemental Ti, Si, and C powders. We present in this paper the results of our investigation. Our current interests are focused on two composites: Ti_3SiC_2/TiC_x and Ti_3SiC_2/SiC. Hot pressing was also performed on selected samples. The volume fractions of different phases from reactive sintered samples were consistent with hot pressed composites.

2. Experimental procedure

Commercially pure elemental Ti, Si and graphite powders were used as starting materials. The particle size of the powders, as well as the mole ratios of the various elements for the different composites, are given in Table I. Samples were ball-milled for 24 hours and then compacted into pellets of 1/2 inch (for pressureless sintering) or disks of 1-1/2 inches in diameter (for hot pressing) in a steel die. Pressureless sintering samples were placed in an alumina boat, covered by graphite powder and sintered in a tube furnace under flowing, gettered (to remove oxygen) argon. The hot pressing was conducted at 1300°C for 1 hour, under flowing argon, at a stress of 27.5 MPa. These samples were wrapped in graphite foil. After sintering and hot pressing, the phases were identified by semi-quantitative XRPD. For selected samples the microstructure was examined by SEM, using both backscattered and secondary imaging modes.

In this paper we report results from three sets of experiments. In the first case, samples with a stoichiometric ratio corresponding to the triple phase (Ti_3SiC_2) were sintered at different temperatures in the range of 1250–1600°C. From this investigation it was determined that 1300°C was the optimum temperature for the synthesis of the triple phase (see Table II). The second set of experiments was conducted to process composites with Ti_3SiC_2 as the matrix and either SiC or TiC as the reinforcement. Five different compositions were investigated. The goal was to produce *in-situ* composites with 25 or 43 mol% SiC or TiC inclusions within the Ti_3SiC_2 matrix. For baseline comparison, stoichiometric Ti_3SiC_2 composition was also investigated. All these samples were sintered at 1300°C for 24 hours. In addition, three samples (43 mol% SiC + 57 mol% Ti_3SiC_2; 100% Ti_3SiC_2; 43 mol% TiC + 57 mol% Ti_3SiC_2) were hot pressed at 1300°C for 1 hour (see Table II). Phase

TABLE I Particle size and composition of constituents used for the samples prepared in this study

		composition (mole ratio)				
	particle size	T + 43%TiC	T + 25% TiC	T*	T + 25%SiC	T + 43%SiC
Ti	44 micron	3	3	3	2.7	2.4
Si[†]	1–5 micron	0.8/0.88	0.9/0.99	1/1.1	1.2/1.32	1.4/1.54
C	2–15 micron	2.2	2.1	2	2.1	2.2

*T = Ti_3SiC_2.

[†] 10 mol% more Si was added for another set of samples to compensate for the Si loss (in the third set of experiments).

TABLE II Sintering and hot pressing parameters used for selected samples in the Ti-Si-C system. Also listed are the crystalline phases identified by XRPD

Compositions	Temperature (°C)	Dwell time (in hours)	Phases Present
Ti_3SiC_2	1250	12	$Ti_3SiC_2/TiC_x/Ti_5Si_3C_x$
Ti_3SiC_2	1600	12	Ti_3SiC_2/TiC_x
Ti_3SiC_2	1600	4	Ti_3SiC_2/TiC_x
Ti_3SiC_2	1300	4	$Ti_3SiC_2/TiC_x/Ti_5Si_3C_x$
$Ti_3SiC_2 + 43\%$ SiC	1300	24	$Ti_3SiC_2/SiC/TiC_x$
$Ti_3SiC_2 + 25\%$ SiC	1300	24	$Ti_3SiC_2/SiC/TiC_x$
Ti_3SiC_2	1300	24	$Ti_3SiC_2/TiC_x/Ti_5Si_3C_x$
$Ti_3SiC_2 + 25\%$ TiC	1300	24	$Ti_3SiC_2/TiC_x/Ti_5Si_3C_x$
$Ti_3SiC_2 + 43\%$ TiC	1300	24	$Ti_3SiC_2/TiC_x/Ti_5Si_3C_x$
	Hot Pressed samples*		
$Ti_3SiC_2 + 43\%$ SiC	1300/27.5 MPa	1	$Ti_3SiC_2/SiC/TiC_x$
Ti_3SiC_2	1300/27.5 MPa	1	$Ti_3SiC_2/SiC/TiC_x$
$Ti_3SiC_2 + 43\%$ TiC	1300/27.5 MPa	1	$Ti_3SiC_2/SiC/TiC_x$

TABLE III Sintering and hot pressing parameters used for samples with additional 10 mol% Si powder. Also listed are the crystalline phases identified by XRPD

Composition	Sintered Temp. (°C)	Dwell Time (in hours)	Phases Present
$Ti_3SiC_2 + 43\%$ SiC + 10%Si	1300	24	$Ti_3SiC_2/SiC/TiC_x$
$Ti_3SiC_2 + 25\%$ SiC + 10%Si	1300	24	$Ti_3SiC_2/SiC/TiC_x$
$Ti_3SiC_2 + 10\%$Si	1300	24	Ti_3SiC_2/TiC_x
$Ti_3SiC_2 + 25\%$ TiC + 10%Si	1300	24	Ti_3SiC_2/TiC_x
$Ti_3SiC_2 + 43\%$ TiC + 10%Si	1300	24	Ti_3SiC_2/TiC_x
	Hot Pressed Samples*		
$Ti_3SiC_2 + 43\%$ SiC + 10%Si	1300/27.5 MPa	1	$Ti_3SiC_2/SiC/TiC_x$
$Ti_3SiC_2 + 10\%$Si	1300/27.5 MPa	1	$Ti_3SiC_2/SiC/TiC_x$
$Ti_3SiC_2 + 43\%$ TiC + 10%Si	1300/27.5 MPa	1	$Ti_3SiC_2/SiC/TiC_x$

identification revealed that there was a loss of Si during sintering. A third set of experiments were conducted using an additional 10 mol% Si to the starting compositions to produce the same target compositions mentioned above [see Table III). Once again five composites were sintered and three were hot pressed under the same set of conditions as those used for the second set of experiments.

3. Results and discussions

According to the thermodynamics and the available phase diagram data [12–17], it is possible to form either single phase or multiple phases providing the starting composition falls into the corresponding phase region. Fig. 1 shows the widely accepted isothermal section at 1200°C of the Ti-Si-C system. The sample compositions chosen for this study are located within the two-phase regions Ti_3SiC_2-SiC and Ti_3SiC_2-TiC_x.

3.1. Preliminary results

The first set of experiments were focused on the influence of heat treatment on the stoichiometric ternary compound, Ti_3SiC_2, by assuming the following reaction would occur at elevated temperatures

$$3Ti + Si + 2C \rightarrow Ti_3SiC_2 \tag{1}$$

However, a large amount of TiC_x is often formed. Another phase, $Ti_5Si_3C_x$ (minor), also forms at the lower sintering temperatures (please see Table II). Based on this observation, a more realistic reaction is as follows:

$$3Ti + Si + 2C \rightarrow Ti_3SiC_2 + Si\ (g) \uparrow + TiC_x + Ti_5Si_3C_x \tag{2}$$

Detailed studies revealed the following trends with respect to the phases Ti_3SiC_2 and TiC_x. As the sintering temperature increased (from 1250 to 1600°C) and the dwell time increased (from 4 to 12 or 24 hours) the relative amount of Ti_3SiC_2 increased and then decreased. It appears that after the optimized sintering parameters are reached, further heat treatment leads to the decomposition of Ti_3SiC_2 according to:

$$Ti_3SiC_2 \rightarrow Si(g) \uparrow + 3TiC_{0.67} \tag{3}$$

The TiC_x phase continues to increase with increasing sintering temperature and dwell time. Eventually it can become the only product phase.

3.2. Compositional effects

After knowing the phase stability of the ternary phase Ti_3SiC_2 and that of TiC_x and $Ti_5Si_3C_x$, five different compositions were chosen to study the effects of stoichiometry. They are numbered as samples 1 to 5.

Sample #3 represents the composition of the pure ternary single phase or the matrix composition Ti_3SiC_2, as in our previous studies. Sample #1 and #2 stand for composites containing (57 mol% $Ti_3SiC_2 + 43$ mol% SiC) and (75 mol% $Ti_3SiC_2 + 25$ mol% SiC) respectively. Similarly, #4 and #5 are used to represent the composite containing (75 mol% $Ti_3SiC_2 + 25$ mol% TiC_x) and (57 mol% $Ti_3SiC_2 + 43$ mol% TiC_x). These samples were sintered at 1300°C for 24 hours in gettered Ar. The results of the crystalline phases identified are summarized in Table II.

For samples enriched in SiC (#1 and #2), three phases were always detected. They were formed based on the following equation:

$$(1-y)(3\mathrm{Ti}+\mathrm{Si}+2\mathrm{C})+(y)\mathrm{SiC} \rightarrow \mathrm{Ti_3SiC_2}+\mathrm{Si(g)}\uparrow+\mathrm{SiC}+\mathrm{TiC}_x \quad (4)$$

The final composite composition from sample #1 ($y = 0.43$) and #2 ($y = 0.25$) fall into the three phase region of Ti_3SiC_2-SiC-TiC_x.

For the stoichiometrical composition Ti_3SiC_2 (#3), the phase observed by XRPD is consistent with the phase diagram. Considering the loss of Si, we found that:

$$3\mathrm{Ti}+\mathrm{Si}+2\mathrm{C} \rightarrow \mathrm{Ti_3SiC_2}+\mathrm{Si(g)}\uparrow+\mathrm{TiC}_x(+\mathrm{Ti_5Si_3C}_x) \quad (5)$$

The products of the above reaction normally fall in to the two-phase region of Ti_3SiC_2-TiC_x. However, with prolonged heat treatment, the minor phase, $Ti_5Si_3C_x$, evolves. In that case, the final composite composition falls into the three-phase region of Ti_3SiC_2-TiC_x-$Ti_5Si_3C_x$.

For samples enriched in TiC, there may be two or three phases present depending on the sintering parameters. The final compositions #4 ($z = 0.25$) and #5 ($z = 0.43$) fall into either the two phase region (Ti_3SiC_2-TiC_x) or the three phase region (Ti_3SiC_2-TiC_x-$Ti_5Si_3C_x$) according to:

$$(1-z)(3\mathrm{Ti}+\mathrm{Si}+2\mathrm{C})+(\mathrm{z})\mathrm{TiC} \rightarrow \mathrm{Ti_3SiC_2}+\mathrm{Si(g)}\uparrow+\mathrm{TiC}_x(+\mathrm{Ti_5Si_3C}_x) \quad (6)$$

From these studies, the influence of composition on the composite properties is clear. The overall amount or volume fraction of the ternary matrix phase Ti_3SiC_2 and that of the SiC reinforcement are increased with increasing Si-content. For TiC_x (and $Ti_5Si_3C_x$ if present), the amount or volume fraction is decreased with increasing Si-content, but is increased with increasing Ti-content.

Fig. 2 presents the effect of the composition on the crystalline phase stability in the Ti-Si-C system under pressureless sintering. The spectrum of $Ti_{2.4}Si_{1.4}C_{2.2}$ (#1) is on the top, Ti_3SiC_2 (#3) in the middle, and $Ti_3Si_{0.8}C_{2.2}$ (#5) on the bottom.

Sintering under pressure helped to prevent the loss of Si and the phase distribution in the composite is therefore favored to have more Ti_3SiC_2 and SiC, but less TiC_x. No trace of $Ti_5Si_3C_x$ was seen by XRPD. Fig. 3 shows the hot pressed XRPD results from the same sample compositions as those in the pressureless sintered ones in Fig. 2. The characterized peaks for Ti_3SiC_2 and SiC are higher in Fig. 3 than those in Fig. 2, while the peak height for TiC_x is considerably lower. The results of the crystalline phases identified in the hot pressed samples are also summarized in Table II.

3.3. 10 mol% addition of Si

Taking the Si loss into account, a set of experiments with an extra 10 mol% Si added to the samples (#1 to #5) have been conducted using the same sintering parameters. The compositions for the new samples are as follows:

1a: (57 mol% $Ti_3SiC_2 + 43$ mol% SiC) + 10 mol% Si
2a: (75 mol% $Ti_3SiC_2 + 25$ mol% SiC) + 10 mol% Si
3a: (100 mol% Ti_3SiC_2) + 10 mol% Si
4a: (75 mol% $Ti_3SiC_2 + 25$ mol% TiC) + 10 mol% Si
5a: (57 mol% $Ti_3SiC_2 + 43$ mol% TiC) + 10 mol% Si

The phase development is different from the previous five compositions. The results are summarized in Table III. The following reactions have been proposed and observed. First, for the SiC-enriched composites:

$$(\text{Sample \#1a and \#2a}) \rightarrow \mathrm{Ti_3SiC_2}+\mathrm{SiC}+\mathrm{TiC}_x \quad (7)$$

The results indicate that their final compositions are in the three-phase region Ti_3SiC_2-SiC-TiC_x and close to the tie-line of Ti_3SiC_2-SiC, because of the high volume fractions of Ti_3SiC_2 and SiC.

For the pure Ti_3SiC_2, the extra Si shifts the final composition from the two-phase region (Ti_3SiC_2-TiC_x) to the three-phase region (Ti_3SiC_2-SiC-TiC_x), with a higher volume fraction of Ti_3SiC_2 phase:

$$(\text{Sample \#3a}) \rightarrow \mathrm{Ti_3SiC_2}+\mathrm{SiC}+\mathrm{TiC}_x \quad (8)$$

For the TiC-enriched composites, their final compositions move into the three-phase region (Ti_3SiC_2-SiC-TiC_x) from the previous two-phase region (Ti_3SiC_2-TiC_x). The volume fraction of Ti_3SiC_2 is higher and the SiC phase appears, while the TiC_x phase decreases (compared to those without excess Si):

$$(\text{Sample \#4a and \#5a}) \rightarrow \mathrm{Ti_3SiC_2}+\mathrm{SiC}+\mathrm{TiC}_x \quad (9)$$

XRPD spectra for pressureless sintered and hot pressed samples with an extra 10 mol% Si are plotted in Figs 4 and 5 respectively. The results of the hot pressed samples are also summarized in Table III.

Comparing the X-ray diffraction results, it can be concluded that:

1. There is an optimized sintering window to achieve the highest amount of the ternary phase Ti_3SiC_2 in terms of sintering temperature and dwell time due to the loss

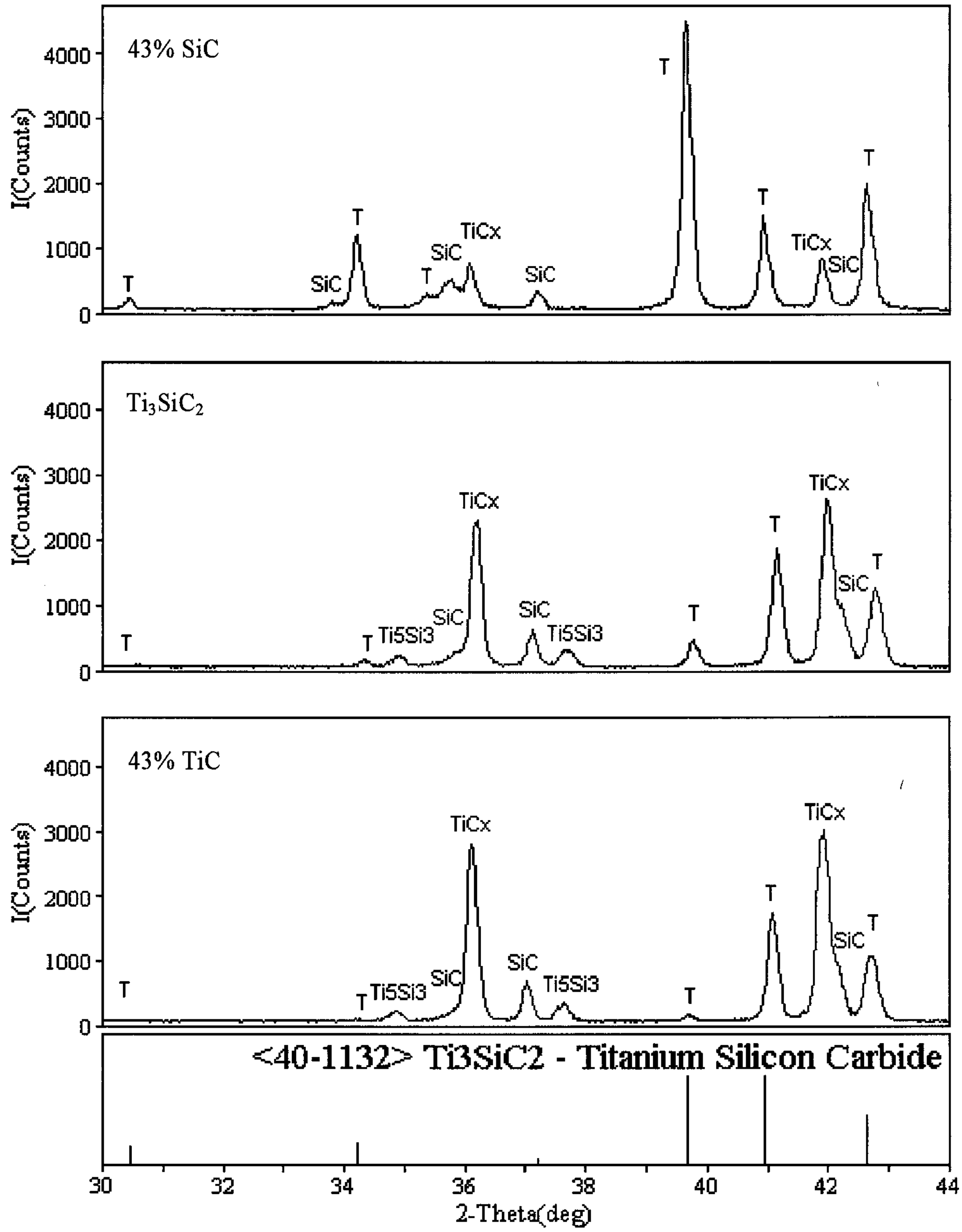


Figure 2 Comparison of the effect of composition on the phase stability of Ti-Si-C composites sintered at 1300°C for 24 hours under Ar.

of Si. Outside this window, the volume fraction of other phases such as TiC_x and $Ti_5Si_3C_x$ increases.

2. The overall amount of both the ternary compound Ti_3SiC_2 and the SiC phase increases with increasing Si-content and with the application of pressure during sintering. Conversely, the overall amount of the TiC_x phase decreases with increasing Si-content and pressure.

3. By adding extra Si powders to account for the Si loss, the sintered phases shift to the three-phase region Ti_3SiC_2-SiC-TiC_x, as expected. No trace of the $Ti_5Si_3C_x$ phase can be found by XRPD. The relative amounts of Ti_3SiC_2 and SiC are higher and that of TiC_x is lower.

Detailed phase analysis showed that the volume fraction of each constituent phase changes with composition, sintering temperature and application of pressure during sintering. Table IV lists the relative ratios of SiC/TiC_x based on the XRPD observations presented in Figs 2 and 3. These results are from the second set of experiments where stoichiometric amount of Ti, Si and C were used. Table V lists the relative ratios of SiC/TiC_x based on the XRPD observations presented in Figs 4 and 5. These results are from the third set of experiments where 10 mol% excess Si was added to the corresponding stoichiometric amount of Ti, Si and C.

The kinetics of the phase changes in the Ti-Si-C system, based on our experimental results, can be addressed as follows:
For the stoichiometric composition of the ternary phase Ti_3SiC_2, it has been observed that:

$$Ti_3SiC_2 \rightarrow Ti_3SiC_2\ (\text{first} \uparrow \text{then} \downarrow) + Si\ (g) \uparrow \\ + TiC_x\ (\uparrow \text{ with Temp. and time}) \quad (10)$$

The loss of Si is the reason that the final composition falls into the two-phase region instead of the solubility region (if there is certain solubility as suggested in the

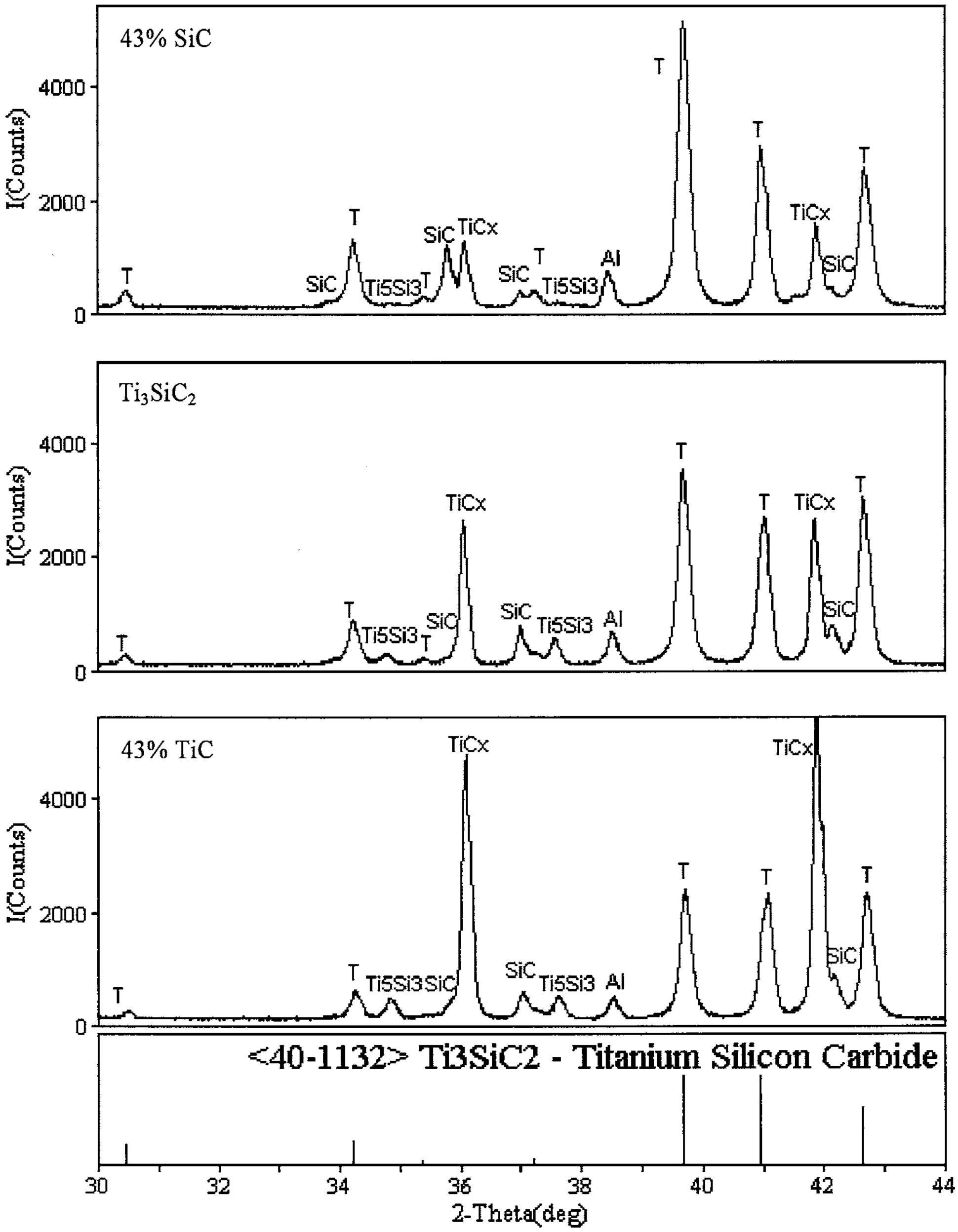


Figure 3 Comparison of the effect of composition on the phase stability of Ti-Si-C composites hot pressured at 1300°C and 27.5 MPa for 1 hour under Ar.

TABLE IV Phase ratio of SiC/TiC$_x$ in the composites with stoichiometric ratios of Ti, Si and C*

	Composition		
	Ti 2.4 Si1.4C2.2	Ti3Si1C2	Ti3Si0.8C2.2
Sintered	1:2	1:7	0
HPed	1:1	1:4	1:8

*Data was taken on the relative peak height of the dominant peak of each phase.

literature [17]) of the ternary compound.

In the SiC-enriched samples, the following phenomena has been observed:

$$\begin{aligned}&Ti_3SiC_2 + SiC\\ &\quad\rightarrow Ti_3SiC_2\ (\text{first}\uparrow\text{then}\downarrow) + Si\ (g)\uparrow\\ &\quad + SiC(\uparrow \text{ with Si content})\\ &\quad + TiC_x(\uparrow \text{ with Temp. and time})\end{aligned} \tag{11}$$

In the TiC-enriched samples:

$$\begin{aligned}&Ti_3SiC_2 + TiC \rightarrow Ti_3SiC_2\ (\text{first}\uparrow\text{then}\downarrow) + Si\ (g)\uparrow\\ &\quad + TiC_x\ (\uparrow \text{ with Temp. and time})\\ &\quad + Ti_3SiC_x(\uparrow \text{ with Temp. and time})\end{aligned} \tag{12}$$

Thus note that in all cases, at low temperature (or short time), the formation of Ti_3SiC_2 is limited. At high temperature (or longer time), decomposition of Ti_3SiC_2 occurs due to Si loss. Thus, there is an optimum set of heat treatment conditions (temperature and time) where the highest volume fraction of Ti_3SiC_2 is formed. Since this optimum is due to kinetic considerations, it is expected that this would be sensitive to physical parameters (e.g. particle size, degree of mixing, etc.). The volume fraction of TiC_x increases with sintering time and temperature and decreases as the amount of Si increases or pressure is applied.

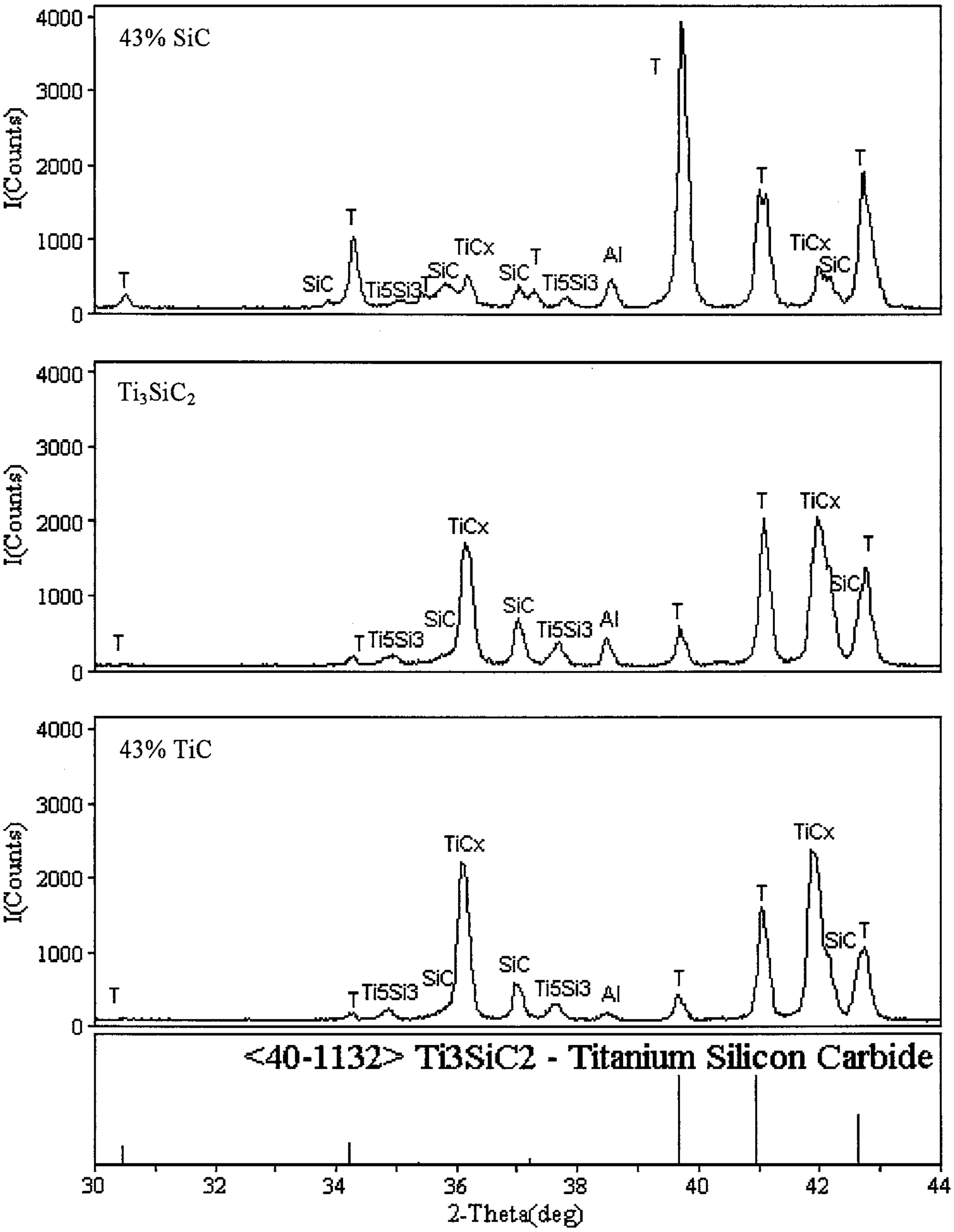


Figure 4 Comparison of the effect of composition with additional 10 mol% Si on the phase stability of Ti-Si-C composites sintered at 1300°C for 24 hours under Ar.

Adding extra Si powder increases the ternary compound and SiC while decreasing the TiC_x phase. The results from the hot pressed samples clearly show that there are three phases mixed together and their characterized peak intensities differ from each other. Although one might expect to see only one (for the stoichiometric, ternary composition) or two phases (for those composite compositions) based on the phase diagram, it is not always the case due to the fact that solid state reactions often do not reach equilibrium during sintering. Further comparison between pressureless sintered and hot pressed samples show that the ternary phase Ti_3SiC_2 and the amount of SiC phase increase with both Si-content and pressure.

In summary, it is clear that the Si is gradually lost at elevated temperatures and such a loss is the reason why it is difficult to form pure, single phase Ti_3SiC_2. The addition of excess Si compensates for this loss. In addition, the application of pressure during sintering also reduces Si loss (presumably by increasing the local partial pressure of Si vapor).

3.4. Microstructural observations

Fig. 6a and b are micrographs of the grain size and shape of the Ti_3SiC_2 phase. The hexagonal morphology of the structure is clearly evident in both figures. The layered nature of the material is shown in 6b. The hexagonal grains appear to be stacked platelets much like scales. Fig. 7a and b are representative, backscattered images of the composite which reveals a non-homogeneous distribution of phases. There appear to be large, isolated regions of the second phase, rather than small well dispersed regions. This could be attributed to non-uniformities in mixing of the initial powders. Fig. 7b is a higher magnification of the rectangular area marked on 7a. The micrograph shows the interface of Ti_3SiC_2 (light region) and TiC (gray region). The black circular

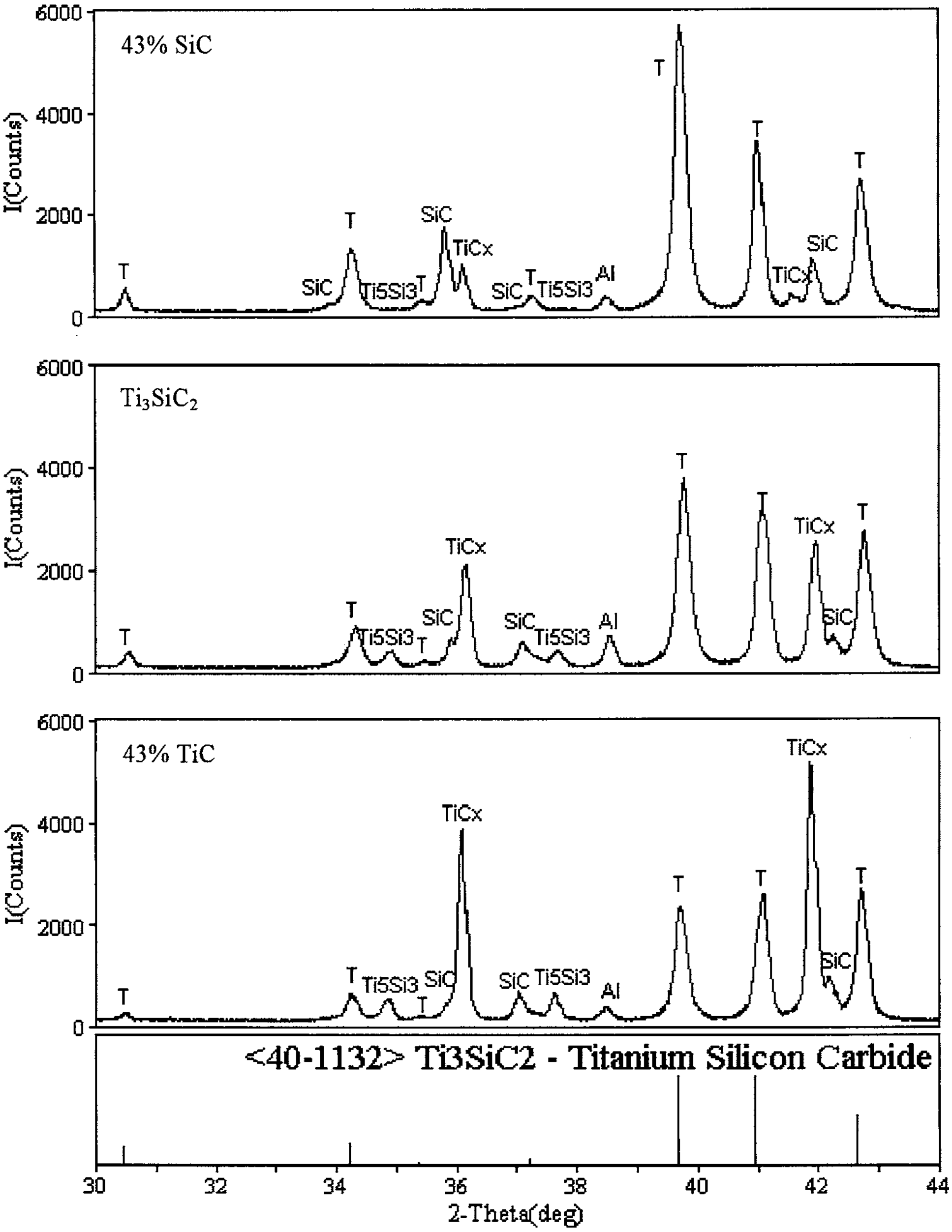
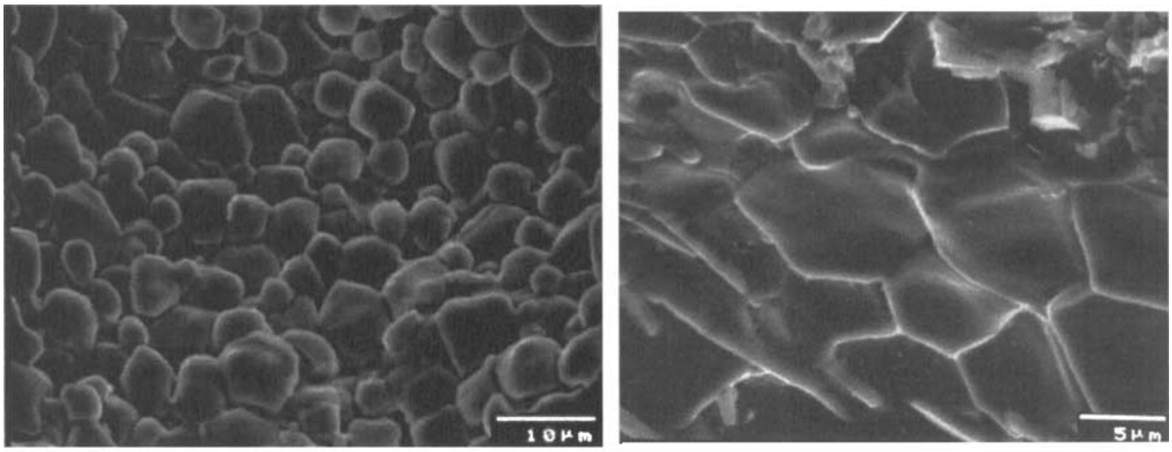
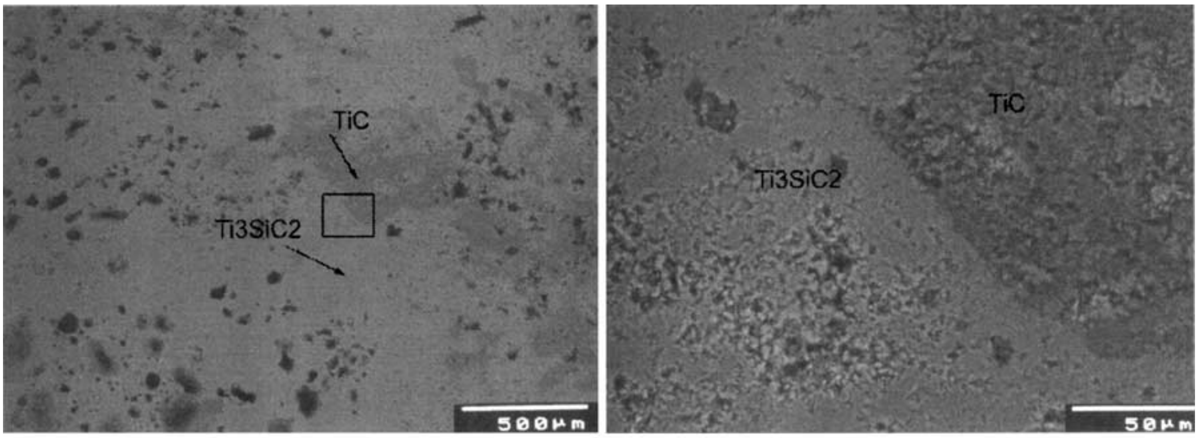


Figure 5 Comparison of the effect of composition on composite with additional 10 mol% Si on the phase stability of Ti-Si-C hot pressed at 1300°C at 27.5 MPa for 1 hour under Ar.



(a) *(b)*

Figure 6 (a) Morphology of the Ti_3SiC_2 phase and (b) Stacked platelets of hexagonal grains.



(a) (b)

Figure 7 (a) Backscattered micrograph showing non uniform phase distribution and (b) High magnification of rectangular region in (a).

TABLE V Phase ratio of SiC/TiC$_x$ in the composites with excess Si*

	Composition		
	Ti 2.4 Si1.54C2.2	Ti3Si1.1C2	Ti3Si0.88C2.2
Sintered	2:3	1:6	0
HPed	2:1	1:3	1:7

*Data was taken on the relative peak height of the dominant peak of each phase.

regions in both micrographs are pores. The microstructures for both phases appear similar and have an ill defined boundary between them.

4. Conclusions

In this study, the feasibility of forming *in-situ* composites with the Ti_3SiC_2 as the matrix phase and SiC or TiC as reinforcements was examined. Knowledge of the phase diagram and simple powder processing techniques were used to form these composites by *in-situ* reactions during sintering. The following conclusions can be drawn from these experiments:

1. Si loss occurs in the temperature range of interest. This leads to a deviation from the target composition and results in phases that can be rationalized in terms of the phase diagram (taking into account Si loss).
2. Si loss can be minimized if experiments are conducted at lower temperature or if samples are hot pressed.
3. Addition of excess Si in the composition can be used to compensate for Si loss during heat treatment.
4. Composites of just Ti_3SiC_2 and TiC were formed rather easily (they formed in all samples with excess Ti or the stoichiometric Ti_3SiC_2 composition)
5. Composites of just Ti_3SiC_2 and SiC could not be formed under the conditions investigated in this study. TiC was always present. However, the volume fraction of TiC could be reduced by increasing Si content in the starting composition or by hot pressing the samples.
6. Microstructure analysis revealed *in-situ* formation of platelets. The boundary between Ti_3SiC_2 and TiC is not well defined.

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